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International Classification:—C08f, g.

COMPLETE SPECIFICATION

New Polymers

We, ROHM & HAAS G.m.b.H., a German Body Corporate, of 16, Darmstadt, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with new chemical compounds and processes for their production, as well as with products derived therefrom.

It has previously been thought that it was not possible to polymerise a compound of the formula

15
$$\text{CH}_2 = \text{CH}-\text{O}-\text{R}-\text{OCO}-\overset{\text{R}_1}{\underset{|}{\text{C}}} = \text{CH}.\text{R}_2$$
 (in which R, R₁ and R₂ have the meanings set out below) to produce a compound having free vinyl-ether groups capable of further reaction.

We have now unexpectedly found however that compounds of the above general formula I when subjected to anionic polymerisation do in fact yield compounds having free vinylether groups. The compounds produced are new compounds which can be further polymerised to produce new synthetic resins as will appear hereinafter.

30 According to the invention therefore we provide as new compounds, polymers comprising repeating units of the general formula:—

35
$$\begin{array}{c} \text{R}_1, \text{R}_2 \\ | \quad | \\ -\text{C}-\text{CH}- \\ | \\ \text{COO}-\text{R}-\text{O}-\text{CH} = \text{CH}_2 \end{array}$$
 (in which R represents a divalent aliphatic

40 group having at least two carbon atoms, which if desired may contain hetero atoms. R₁ represents hydrogen or an alkyl group and R₂ represents hydrogen, an alkyl or aryl group).

45 In the above general formula II, the group

R is preferably an ethylidene or butylidene group and it is preferred that R₁ be a methyl group and R₂ be hydrogen.

According to a feature of the invention we provide a process for the production of a 50 polymer of the general formula II specified above in which a compound of the formula

$$\text{CH}_2 = \text{CH}-\text{O}-\text{R}-\text{OCO}-\overset{\text{R}_1}{\underset{|}{\text{C}}} = \text{CH}.\text{R}_2$$
 55 (where R, R₁ and R₂ have the above stated meaning) is subjected to anionic polymerisation.

The polymerisation process is preferably carried out in liquid ammonia, and there- 60 fore at temperatures of below -34°C. The liquid ammonia preferably contains an alkali metal, for example, potassium.

The polymerisation should of course be carried out substantially in the absence of 65 substances which inhibit polymerisation particularly compounds having free hydroxyl groups such as, for example, glycol-mono-vinylether.

As examples of compounds which may 70 be used as starting materials in the process according to the invention may be mentioned vinyl-glycol methacrylate (β-vinyloxy-ethyl-methacrylate) and δ-vinyloxy-butylmethacrylate. The former compound may be pre- 75 pared, for example, by the alcoholysis of a methacrylic acid ester, for example methyl methacrylate with glycol-monovinylether, the glycol-monovinylether used conveniently being prepared by the reaction of acetylene 80 with glycol.

The process according to the invention for the production of the polymers of the general formula II above-specified may if desired, be modified by carrying out the anionic 85 polymerisation in the presence of other ethylenically unsaturated polymerisable monomers, thus producing products having different properties.

The new polymers provided according to 90

the present invention have the valuable property that they can be further polymerised or copolymerised to give new synthetic resins, for example by cationic or radical polymerisation with or without other polymerisable monomers.

Thus, according to the invention it is possible to polymerise the new polymers according to the invention by radical or cationic polymerisation with or without other ethylenically unsaturated polymerisable monomers to give new synthetic resins having valuable properties. As examples of other polymerisable monomers with which the new polymers according to the invention can be polymerised may be mentioned, monomeric acrylic and methacrylic acid esters, for example methyl methacrylate, and styrene as well as low molecular polymers of said polymerisable monomers which contain unsaturated double bonds, for example dimers, trimers and tetramers of esters of acrylic and methacrylic acids. Suitable catalysts for effecting the polymerisation include, for example, azodiisobutyric acid nitrile, benzoyl peroxide and boron fluoride. The dense cross-linkage of the synthetic resins so produced makes them hard and substantially insoluble in the usual synthetic resin solvents; they also show little tendency to swell in such solvents and can be used with advantage in the production of dental prostheses. By varying the proportion between the new polymerisable compounds according to the invention and the monomer or polymer with which it is to be copolymerised it is possible to obtain a range of products with will have properties depending on the degree of cross-linking in the copolymer produced. Thus by varying the proportions of the reaction components one can produce a copolymer having any desired mechanical characteristics. The polymerisation may also be carried out in the presence of high molecular weight polymers of said polymerisable monomers e.g. of esters of acrylic and methacrylic acid, which do not contain unsaturated double bonds but which act as fillers, instead of or in addition to the polymerisable monomers or low molecular polymers thereof.

The new polymers according to the invention may be reacted with compounds reactive therewith other than by radical or cationic polymerisation. Thus, in general,

Yield: 35 g. η sp/c = 0.011 litre. g. ⁻¹ 20°C (in chloroform)					
found	60.5% C	8.2% H	26.3% H	26.3%	-O-CH=CH ₂
calculated	61.5% C	7.7% H	27.5% H	27.5%	-O-CH=CH ₂

The polymer is readily soluble in acetone, benzene, chloroform or ethyl acetate.

20 g of the polymer thus produced are dissolved in 100 g of methyl methacrylate mixed with 0.01 g of azodiisobutyric acid nitrile and polymerized for 16 hours at 60°C and for 6 hours at 100°C. One obtains a

they may be reacted with compounds containing groups reactive to vinyl ether groups, for example, hydroxyl, carboxyl or thiol groups, by condensation or addition reactions. In particular, they may be reacted with compounds containing a number of such reactive groups such as polyester resins, for example a condensation product obtained the reaction of adipic acid with ethylene glycol which contain free hydroxyl and/or carboxyl groups to give end-products having valuable properties. Such a reaction can for example be carried out in the presence of an acid catalyst, preferably a mineral acid, for example sulphuric acid. By the addition of hydrogen sulphide across the free vinyl-ether groups -SH group-containing polymers can be obtained, which cannot be obtained by ionic or radical polymerisation of monomers and which can, for example, be used as ion-exchange resins or as polymerisation regulators. In addition to hydrogen sulphide itself, a compound yielding hydrogen sulphide may be used, e.g. thioamides, in particular thioformamide and thioacetamide.

In order that the invention may be well understood the following examples are given by way of illustration only:—

EXAMPLE 1

150 ccs. of ammonia dried over caustic alkali are condensed in an apparatus sealed off against atmospheric moisture, which is equipped with an agitator, a thermometer, and an inlet- and exhaust tube for ammonia. 0.5 g of metallic potassium are then dissolved in the liquid ammonia and 40 g of β -vinyl-oxy-ethylmethacrylate (BP₁₀ = 85°C, n_D^{20} = 1.448, OH = 0.0 %) is allowed to flow into the deep-blue solution. The temperature is kept at -35°C by cooling. The blue solution immediately loses its colour and a colourless or weak yellow polymer precipitates. The total reaction time is about 10 minutes. The catalyst is then inactivated by the addition of 5 ccs. of water and the ammonia evaporated. The polymer is dissolved in 100 ccs of acetone, precipitated by diluting with water, washed free of alkali with water and dried in vacuo at room temperature over calcium chloride. The drying can also take place at an elevated temperature for example 70°C, without the cross-linking setting in.

clear, hard, still thermoplastically mouldable polymer which swells only slightly in chloroform.

EXAMPLE 2

A solution of 20 g of β -vinyl-oxy-ethylmethacrylate in 100 g of anhydrous ether is mixed with 5 g of a 20% dispersion of

sodium in paraffin oil. The mixture is left standing with occasional shaking for 1 day under dry nitrogen. There is then added thereto 10 ccs of butanol and after the grey colour of the sodium has disappeared the polymer is filtered off. This is dissolved in benzene, precipitated with methanol and dried in vacuo.

Yield: 8g. η sp/c = 0.015 litre. g⁻¹ 20°C (in chloroform)

found: 61.3% C 7.61% H
calculated 61.5% C 7.7% H

2 g. of this polymer was polymerised with 8 g of acrylonitrile for 8 hours at 60°C

found: 64.3% C 8.3% H
calculated 65.2% C 8.7% H

- 30 The polymer thus produced is polymerized for 15 hours at 60°C and 7 hours at 100°C with 2.5 g of styrene and with the addition of 0.25 g of benzoyl peroxide. The copolymer is somewhat cloudy. It is less brittle than pure polystyrene and only still slightly swellable in chloroform.

EXAMPLE 4

- 5 g. of β -vinyl-oxy-ethyl-methacrylate anionically polymerized according to Example 1 are dissolved in 10 ccs of styrene and cast into a film. The film on treatment with gaseous boron trifluoride in an anhydrous atmosphere polymerizes to a hard insoluble layer.

EXAMPLE 5

- 1 part of a condensation resin prepared from adipic acid and ethylene glycol with a mean molecular weight of 1100, which has end hydroxyl groups, is mixed with 2 parts of the anionic prepolymer produced according to Example 1 dissolved in ethyl acetate and mixed with 0.006 parts of sulphuric acid (dissolved in acetone) as catalyst. The mixture is immediately cast into films. These are bone-dry after 10 minutes and cannot be scratched with the fingernail after 30 minutes. After 45 hours they are only still very slightly swellable in ethyl acetate.

EXAMPLE 6

- 15.6 g of an anionic prepolymer prepared according to Example 1 from β -vinyl-oxy-ethyl-methacrylate is dissolved in 85 g of dioxan and a solution of 20 g of thioglycolic acid in 50 g dioxan is then slowly added thereto. A mild heating takes place. The mixture is held at about 80°C for 1 day, and the polymer then precipitated by pouring the mixture into 1 litre of water. It is then repeatedly dissolved in acetone and precipitated with water. The polymer was then dried at 40°C. It has a sulphur content of 14.2% S.

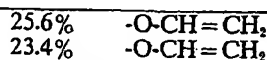
WHAT WE CLAIM IS:—

1. As new compounds, polymers comprising repeating units of the general formula:—

using 0.01 g of benzoyl peroxide as catalyst. There is obtained a hard polymer, insoluble in organic solvents.

EXAMPLE 3

In the same manner as in Example 1 one allows 5.9 g. of δ -vinyl-oxy-butyl-methacrylate to flow into a solution of 0.2 g of potassium in 150 ccs. of ammonia. The monomer, which is difficultly soluble in ammonia, gradually changes into a viscous mass. After evaporating off the ammonia the polymer is dissolved in ether, filtered, precipitated with methanol and dried in vacuo



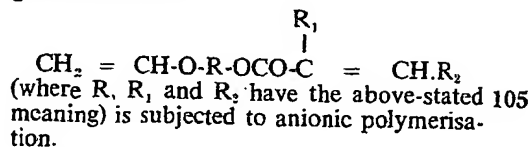
(in which R represents a divalent aliphatic group having at least two carbon atoms, which if desired may contain hetero atoms, R₁ represents hydrogen or an alkyl group and R₂ represents hydrogen, an alkyl or aryl group).

2. Polymers as claimed in Claim 1 in which R represents an ethylidene or butylidene group.

3. Polymers as claimed in either Claim 1 or Claim 2 in which R₁ represents a methyl group.

4. Polymers as claimed in any of Claims 1-3 in which R₂ represents hydrogen.

5. A process for the production of the polymers of the general formula specified in Claim 1 in which a compound of the general formula:—



6. A process as claimed in Claim 5 in which the polymerisation is carried out in liquid ammonia.

7. A process as claimed in Claim 6 in which the polymerisation is effected at a temperature of below -34°C.

8. A process as claimed in Claim 6 or Claim 7 in which an alkali metal is present in said liquid ammonia.

9. A process as claimed in Claim 8 in which said alkali metal is potassium.

10. A process as claimed in any of Claims 5-9 in which β -vinyl-oxy-ethyl-methacrylate or δ -vinyl-oxy-butylmethacrylate is used as starting material.

11. A process as claimed in any of Claims 5-10 in which the polymerisation is carried out in the presence of ethylenically unsaturated polymerisable monomers other than those of the formula specified in Claim 5.

12. A process for the production of polymers as claimed in any of Claims 5-11 substantially as herein described with reference to any one of examples 1-3.
- 5 13. New polymers as claimed in any of Claims 1-4 whenever prepared by a process as claimed in any of Claims 5-12.
14. A process for the production of new synthetic resins which comprises subjecting
10 a polymer as claimed in any of Claims 1-4 to radical or cationic polymerisation if desired in the presence of other ethylenically unsaturated polymerisable monomers.
- 15 15. A process as claimed in Claim 14 in which the polymerisation is carried out in the presence of high molecular weight polymers of said monomers.
16. A process as claimed in Claim 14 or Claim 15 in which said monomers is/are
20 ester(s) of acrylic and/or methacrylic acid.
17. A process as claimed in Claim 14 in which the monomer is styrene.
18. A process as claimed in any of Claims 14-17 in which the polymerisation is effected
25 in the presence of one of the following catalysts: azodiisobutyric acid nitrile, benzoyl peroxide, and boron fluoride.
19. A process for the production of new synthetic resins from the polymers claimed
30 in any of Claims 1-4 substantially as herein described with reference to any one of examples 1-4.
20. New synthetic resins when prepared by a process as claimed in any of Claims
35 14-19.
21. A process for the preparation of new compounds derived from polymers as claimed in any of Claims 1-4 which comprises reacting said polymers with compounds capable of reaction therewith,
40 mainly by addition across said free vinyl ether groups.
22. A process as claimed in Claim 21 in which the compounds capable of reaction with the new polymers are polyester resins.
45
23. A process as claimed in Claim 22 in which said polyester resin is a condensation product between adipic acid and ethylene glycol.
24. A process as claimed in any of Claims 50 21-23, in which the reaction is effected in the presence of an acid catalyst.
25. A process as claimed in Claim 24 in which said acid catalyst is a mineral acid.
26. A process as claimed in Claim 25 in 55 which said mineral acid is sulphuric acid.
27. A process as claimed in Claim 21 in which hydrogen sulphide is added across said free vinyl ether groups.
28. A process for the production of new 60 compounds derived from the polymers claimed in any of Claims 1-4 substantially as herein described with reference to either Example 5 or Example 6.
29. New compounds whenever prepared 65 by a process as claimed in any of Claims 21-28.

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